Nematic molecular core flexibility and chiral induction

Tzu-Chieh Lin¹, Ian R. Nemitz¹, Christopher J. McGrath², Christopher P. J. Schubert²,

Hiroshi Yokoyama³, Robert P. Lemieux³, and Charles Rosenblatt¹,a)

¹Department of Physics, Case Western Reserve University, Cleveland, Ohio  44106   USA

²Department of Chemistry, Queen’s University, Kingston, Ontario K7L 3N6   Canada

³Liquid Crystal Institute, Kent State University, Kent, Ohio  44242   USA
Abstract

Electroclinic measurements, in which an applied electric field $E$ induces a rotation $\theta \propto E$ of the liquid crystal director about the electric field axis in a chiral environment, were performed on several configurationally achiral liquid crystals in the presence of an imposed helical director profile.

This imposed twist establishes a chiral symmetry environment for the liquid crystal. It was observed that a conformationally racemic mesogen possessing a flexible phenyl benzoate core exhibits a measurable electroclinic response in the nematic phase. On the other hand, when the phenyl benzoate mesogen is mixed with a mesogen containing a rigid, configurationally achiral core (fluorenone), or with a racemic dopant with an axially chiral core that mimics a mesogen having rigid right- and left-handed conformations (2,2’-spirobiindan-1,1’-dione), the magnitudes of the electroclinic responses were found to decrease sharply, apparently going to zero when extrapolated to the pure 2,2’-spirobiindan-1,1’-dione or fluorenone limit. Note that neither of these additives possesses a nematic phase. The results suggest that the flexibility of the core and its ability to deracemize conformationally in order to compensate the elastic energy cost of the imposed twist is the primary mechanism behind the observed electroclinic response.
Chiral phenomena are pervasive in nature [1]. In addition to effects such as circular dichroism and optical rotatory power, chirality manifests itself within the realm of liquid crystals in many ways, including a ground-state director twist in the nematic — actually the cholesteric — phase [2], a spontaneous electrical polarization in the chiral smectic-C phase [3], and spontaneous chiral symmetry breaking [4,5,6,7]. When a chiral dopant is added to a configurationally achiral liquid crystal, chirality is induced in the nearby mesogens, resulting in chiral physical properties for the mixture [8]. The degree of chiral induction depends intimately on the nature of intermolecular non-covalent interactions between the dopant and the liquid crystal, and one can envision different mechanisms for chirality transfer. For example, if the liquid crystal is a racemic mixture of left and right-handed conformers, chiral induction may occur by a conformational deracemization in which the dihedral angular distribution of the aromatic core (or some other appropriate structural unit) is no longer symmetric about zero [9]. Another possible mechanism involves a chiral dopant-induced orientational deracemization of the conformers, whereby the orientational distribution functions of the right and left-handed enantiomers are no longer identical [10,11]; in this scenario, the number distribution of conformers may remain racemic, although this is not required. Thus one can have a combination of both conformational and orientational deracemization.

Recently we examined a macroscopic mechanical torsional strain imposed on a
configurationally achiral liquid crystal — this corresponds to an imposed twist of the liquid crystal director \( \mathbf{n} \) by constructing a cell in which there is an azimuthal angle \( \theta_0 \neq 0 \) between the alignment layers’ easy axes [12]. We found that this arrangement results in an electroclinic effect (ECE), wherein an applied electric field \( E \) induces a rotation \( \Delta \theta \propto E \) of the local director about the electric field direction. We concluded that \( \Delta \theta \) is maximum at the two bounding substrates as \( \mathbf{n} \) can deviate sharply over a few molecular diameters from the easy axes, producing an effective short helical pitch local twist environment at the substrates. This is because the twist elastic energy attempts to promote a uniform director orientation, and the resulting torque “pulls” the director by a small angle away from the easy axes. The key point is that the electroclinic effect, which requires a chiral environment, occurs where \( d\theta/dz \neq 0 \) and is largest where \( d\theta/dz \) is large; here \( \theta \) is the azimuthal orientation of the planar-aligned director and the \( z \)-axis is perpendicular to the substrates. In fact, when the pitch of a chirally-doped liquid crystal is adjusted to provide a director rotation across the cell corresponding exactly to the imposed angle between the two easy axes, \( \mathbf{n} \) becomes parallel to the easy axes at the two surfaces and the electroclinic effect becomes immeasurably small [13].

The existence of an electroclinic effect in a twist cell is permissible on symmetry grounds, for which chirality is required. The mechanisms governing the effect, however, are much less well understood. In Ref. 12 we suggested that the system could reduce its overall energy by undergoing
partial conformational deracemization of the aromatic core in which the energy barrier is only \( \sim 0.8 \) \( k_B T \) for the liquid crystal 9004 (Fig. 1a). This would reduce the macroscopic twist elastic energy cost, in exchange for an increase in the entropy cost associated with the conformational deracemization. Using estimates for the liquid crystal’s physical parameters [12], the results of our simple model were in good agreement with the experimental electroclinic coefficient. But is this the only possibility? As described above, other symmetry-allowed scenarios that could result in a linear electroclinic effect exist. Here we examine experimentally two of these possibilities: i) an orientational deracemization of the right and left-handed conformers, in which the numbers of left and right-handed conformers remain the same in the presence of the imposed twist, but conformers of opposite handedness adopt different orientational distributions in the helical environment, and ii) a reduction from D\(_2\) to C\(_2\) point symmetry on application of an electric field to a twisted director arrangement, even if the molecules are achiral [14].

We examined experimentally these two scenarios by i) using a racemic mixture of a dopant with an axially chiral core that mimics a configurationally achiral mesogen with “rigid” right- and left-handed conformers whose energy cost to conformationally switch handedness would be \( \sim 100 \) \( k_B T \) according to bond dissociation energy tables, and ii) using a configurationally achiral mesogen with a rigid and conformationally achiral core. Since neither of the two compounds exhibits the requisite nematic phase for the experiment, we measured the electroclinic coefficients using
mixtures of each of these compounds in the liquid crystal 9004. Our central result is that, on extrapolation to 0 wt-% 9004, neither of these compounds showed a measurable electroclinic coefficient, suggesting that their contributions to the electroclinic effect are much smaller than what we believe is the likely mechanism, viz., a macroscopic helical twist-induced conformational deracemization of the chiral conformers.

A pair of indium-tin-oxide (ITO) coated glass slides was used as the substrates for each cell. After the ITO glass was cleaned in detergent, acetone, and ethanol, the planar-alignment material RN-1175 (Nissan Chemical Industries) was spin coated on the substrates. The coated substrates were prebaked at 80°C for 5 min to form the polyamic acid, and then at 250°C for 60 min to create the polyimide. The slides were then rubbed unidirectionally using a commercial rubbing cloth to create an easy axis on each substrate for alignment of the director. Two substrates were placed together, separated by spacer beads of diameter 4 µm, and cemented, with their easy axes rotated by an angle $\theta_0 = (30 \pm 1)^\circ$ with respect to each other to create a right-handed twist cell. The cells had an air gap $d$ between the two alignment layers which was found to be $d = (4.1 \pm 0.2) \mu m$ for all cells, as measured by optical interferometry.

For scenario i, orientational deracemization of the right and left-handed conformers, eight cells were filled in the isotropic phase with different concentrations $c$ of the racemic 2,2’-spirobiindan-1,1’-dione (RS)-1 [15] (Fig. 1b) in the liquid crystal 9004: 0, 9.0, 16.5, 23.5, 33.7,
49.6, 59.4, and 72.0 wt-% mixture of (RS)-1 in the liquid crystal 90O4. [Pure 90O4 has a phase sequence: Iso – 83° – N – 70° – Sm-A – 62° – Sm-C – 50° – Sm-B – 35° – Cryst.] The 2,2'-spirobiindan-1,1'-dione racemate does not form a liquid crystalline phase, but it mixes well in 90O4 using chloroform as a solvent. The chloroform then was removed by baking for 4h at 75°C. The presence of (RS)-1 depresses the clearing point of 90O4 from 83° at c = 0 to 55° at c = 72 wt-%, along with the expected increase in the size of the biphasic region δT_{biphasic}, reaching δT_{biphasic} ~ 2.4° at c = 72 wt-%. Interestingly, despite the depression of the nematic – isotropic transition temperature with increasing c, the temperature width ΔT_{Nem} of the metastable nematic phase remains wide, approximately 9.7°, even at c = 72 wt-% (RS)-1. Owing to phase separation, which occurs more rapidly at higher (RS)-1 concentrations, we chose to perform all measurements in the region c ≤ 72.0 wt-% where at least a uniform but metastable nematic phase could be achieved during the course of the experiment. The liquid crystal-filled twisted cells were mounted between polarizers, where details of the experimental geometry are given in detail in Ref.12. An ac voltage at frequency f = 100 Hz was ramped from 0 to 7.3 V_{rms} over 180 s, and both the ac and dc optical signals at the detector were recorded. The intensity ratio I_{ac} / 4I_{dc}, which is proportional to the induced director rotation Δθ, would be identically equal to Δθ at f = 0. That I_{ac} / 4I_{dc} is less than Δθ for f ≠ 0 is due to viscoelastic effects that occur when a bulk director rotation is driven by the surface layers. The quantity I_{ac} / 4I_{dc} vs. E was measured at frequency f = 100 Hz for each
concentration at several different temperatures within the nematic range, and a typical result is shown in Fig. 2.  Figure 3 shows the slopes $d(I_{ac} / 4I_{dc}) / dE$, which is proportional to the electroclinic coefficient $e_c [\equiv d\Delta \theta / dE \text{ at } f=0]$, as a function of temperature.  As is readily apparent, the electroclinic response decays continuously with increasing (RS)-I concentration $c$, apparently going toward a very small value — at least much smaller than that of the pure 9OO4 mesogen — as $c \to 1$.  [As an aside we note that the magnitude of $e_c$ for the pure 9OO4 is larger by nearly an order of magnitude than that reported in Ref. 12.  The reason for this is that the measurements reported herein were performed at $f = 100$ Hz and $\theta_0 = 30^\circ$, and those in Ref. 12 at $f = 1$ kHz and $\theta_0 = 20^\circ$.  See inset, Fig. 2, Ref. 12.]

For scenario ii, we examined mixtures of the fluorenone mesogen C10 (Fig. 1c), which has a board-like, conformationally achiral core and a phase sequence Iso – 87º – Sm-C – 62º – Cryst, in the liquid crystal 9OO4 [16].  Here six cells having concentrations 0, 15.0, 25.1, 34.2, 49.8, and 58.3 wt-% C10 in 9OO4 were filled in the isotropic phase.  Over this concentration range the clearing temperature of the mixture decreased from 83º at $c = 0$ wt-% to 72º at $c = 58.3$ wt-%, and the temperature width $\Delta T_{nem}$ of the nematic phase decreased from 13º to approximately 1º.  Thus, the experiment in the nematic phase was limited to C10 concentrations $c \leq 58.3$ wt-%.  As before, electroclinic measurements were performed at frequency $f = 100$ Hz.  Figure 4 shows a typical result for $I_{ac} / 4I_{dc}$ vs. $E$, and Fig. 5 shows the slopes $d(I_{ac} / 4I_{dc}) / dE$, which again is proportional
to the electroclinic coefficient $e_c \equiv \frac{d\Delta \theta}{dE}$ at $f = 0$. In this case the electroclinic response
\[ d\left(\frac{I_{ac}}{4I_{dc}}\right)/dE \] appears to decrease linearly with $c$, extrapolating to zero at $c = 100$ wt-%.

The data seem to indicate that the electroclinic response either would vanish or become very small for both cases i and ii in the extrapolated limit where only the fluorenone $\text{C10}$ or the $2,2'$-spirobiindan-1,1'-dione ($\text{RS}$)-1 were present. This would suggest that molecules possessing rigid cores, whether they are conformationally achiral or racemic mixtures of “rigid” right- and left-handed molecular conformations, do not couple sufficiently to the twisted director environment to produce a measurable electroclinic response. Greco and Ferrarini, however, have modeled molecular properties such as shape, dipole moment, and polarizability at the atomic level to calculate electroclinic coefficients for a variety of rigid prototypical molecular structures [14]. They obtained values for $e_c$ that are similar to those found experimentally for the non-rigid 9004 mesogen in Ref.12, from which they concluded that a) a twisted director environment in a liquid crystal composed of rigid, conformationally achiral molecules can result in a significant nematic ECE and b) the electroclinic contributions of rigid and opposite enantiomers can differ in a twisted environment. In our experiments, we attempted to examine assertion $a$ with $\text{C10}$ and $b$ with ($\text{RS}$)-1. On the surface the experimental results reported herein would seem to conflict with the magnitudes of $e_c$ obtained in these calculations, although on symmetry grounds the mechanisms suggested by Greco and Ferrarini are permitted. Where might the inconsistencies lie? First, the
experiments reported herein were performed over only a limited — albeit large — concentration region for two very specific rigid dopant molecules. The interactions of the rigid dopants with the host 9004 may be qualitatively different in the limit that the dopant concentrations $c \to 100$ wt-%. And, of course, the calculations were performed only for single-component “model” molecules, none of which is similar in structure with the two rigid dopants. Second, the presence of the dopants can affect the mixture’s mechanical properties, particularly the twist elasticity $K_{22}$ and the azimuthal anchoring strength coefficient $W_2$, both of which play an important role in the ECE [17]. For example, if the rigid dopant molecules were preferentially adsorbed at the surfaces and were to result in a significant enhancement of $W_2$, then the misalignment of the director from the easy axes would be reduced, resulting in an increased effective surface pitch $p_s$ and therefore a reduced electroclinic coefficient. Third, despite the presence of transverse carbonyl groups that occur in both dopants and in the 9004, the electrical properties of the dopants are not identical to the host. Despite these caveats, however, it is difficult to ignore the clear trends in Figs. 3 and 5 that suggest that the rigidity of the dopant cores plays a large role in suppressing the electroclinic response, and therefore conformational deracemization in a twisted environment are likely the more important contributor. To be sure, conformational deracemization can occur in the tails of the two rigid-core dopants and 9004 (not just in the 9004 core), thus contributing to an ECE [10]. This effect was not considered in Ref. 12 and requires a much more robust theoretical treatment than presented.
Chirality transfer continues to be an open problem [18]. Although the electroclinic effect in a twisted nematic cell was first explained by a mechanism involving the conformational deracemization of a phenyl benzoate core [12], recent calculations suggest that other symmetry-permitted mechanisms that couple the molecular structure to the director twist may play a role. The experimental results herein indicate that the ECE becomes very small for two specific rigid-core-but-flexible-tail molecules when extrapolated to 100 wt-% concentrations. Given the structural differences between the flexible core liquid crystal 9004 and the rigid core dopants, the data would seem to suggest that conformational deracemization of the core is likely to be the main — although not necessarily the only — contributor to the ECE.

**Acknowledgments** The authors thank James Scheuermann and Joel S. Pendery, for assistance with the experiments and Prof. Alberta Ferrarini and Prof. Rajratan Basu and for invaluable discussions. The Queen’s University group was supported by the National Sciences and Engineering Research Council of Canada. HY was supported by the Ohio Research Scholar program, the State of Ohio. At Case Western Reserve, the data collection and analysis were supported by the U.S. Department of Energy’s Materials Chemistry Program under Grant No. DE-FG02-01ER45934 and the experimental construction, computer interfacing and software
development by the National Science Foundation’s Condensed Matter Physics and Solid State and Materials Chemistry Programs under Grant No. DMR-1065491.
Appendix A

Here we define the conformational and orientational deracemization mechanisms more formally. Let \( \rho^D(r, \omega) \) and \( \rho^L(r, \omega) \) be the density functions of the D- and L-enantiomers at the point \( r \), where the orientation \( \omega = (\omega_1, \omega_2, \ldots, \omega_n) \) describes the complete set of bond vectors of the molecule. The density function can be written as the product of the local number density and the orientational distribution function: \( \rho^D(r, \omega) = \rho^D_0(r) f^D(\omega) \) and \( \rho^L(r, \omega) = \rho^L_0(r) f^L(\omega) \). In general, deracemization can be associated with \( \rho^D_0(r) \neq \rho^L_0(r) \) or \( f^D(\omega) \neq f^L(\omega) \). The former can correspond to either spatial segregation of enantiomers, where the total number of D- and L-enantiomers are the same, or to conformational deracemization where the total numbers of enantiomers differ. If both number densities are identical, orientational deracemization is special cases of phase space deracemization and corresponds to \( f^D(\omega) \neq f^L(\omega) \). Restricting our attention to a rigid chiral molecule of arbitrary shape, we are left with two vectors \( \omega = (\omega_1, \omega_2) \); a rigid rod-like molecule has just one vector \( \omega \). In a twisted nematic liquid crystal, the orientational distribution functions are \( f^D(\omega) = f_0^D(\omega) + a(n \cdot \nabla \times n)(n \cdot \omega)^2 \) and \( f^L(\omega) = f_0^L(\omega) - a(n \cdot \nabla \times n)(n \cdot \omega)^2 \). The second term on the right-hand-side describes the effect of uniform twist as given by the twist deformation \( n \cdot \nabla \times n \). The coefficient \( a \) is the pseudo-scalar describing the strength of guest-host chiral coupling, and is related to the chiral twisting power of the molecule with respect to the host. Obviously, the sign before \( a \) is opposite for D- and L-
enantiomers. Put in different terms, the orientational deracemization can be understood to modify
the respective orientational order parameters: $S_d = S + \frac{4}{15} a(n \cdot \nabla \times n)$ and
$S_L = S - \frac{4}{15} a(n \cdot \nabla \times n)$. 
Figures

1. Chemical structure of a) 9OO4, b) 2,2’-spirobiindan-1,1’-dione (RS)-1, and c) fluorenone C10

2. $I_{ac}/4I_{dc}$, which is proportional to the induced director rotation $\Delta \theta$, vs. applied electric field for a 59.4 wt-% (RS)-1 mixture in 9OO4.

3. The derivative $d(I_{ac}/4I_{dc})/dE$, which is proportional to the electroclinic coefficient $e_z$, vs. concentration $c$ of (RS)-1 in 9OO4. For each concentration several measurements were made within the concentration-dependent nematic phase region having width $\Delta T_{Nem}$. The larger response occurs at lower temperatures within the nematic region. Typical error bars are shown.

4. $I_{ac}/4I_{dc}$ vs. applied electric field for a 50 wt-% C10 mixture in 9OO4.

5. The derivative vs. concentration $c$ of C10 in 9OO4.
Figure 1
Figure 2
Figure 3
Figure 4

The graph depicts the relationship between $I_{ac}/4I_{dc}$ and $E_{rms}$ ($V \mu m^{-1}$). The data points show a linear trend as $E_{rms}$ increases.

Figure 4
Figure 5


10 C. Greco and A. Ferrarini, unpublished

11 H. Yokoyama (unpublished)


